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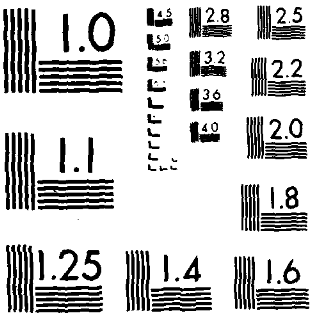

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Experimental techniques were developed and used for the unambiguous identification of donors in high-purity epitaxial GaAs, InP and related compounds. Magnetic fields up to 20 T and high-resolution submillimeter spectroscopy were used to distinguish the Zeeman transitions 1s 2p(m=-1) of each different donor and to describe the dependence of the line shape on field intensity. Transmutation doping was used to distinguish Se and Ge donors, molecular beam epitaxy to distinguish Sn. These methods were extended to InGaAs near millimeter wavelengths. Finally, the magnetic field dependence of the spin doublet in GaAs was measured. A donor was seen in InP

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IMPURITY AND DEFECT CHARACTERIZATION IN EPITAXIAL GaAs InP AND THE TERNARY AND QUATERNARY COMPOUND SEMICONDUCTORS

Kenneth J. Button, Principal Investigator
Mohammed N. Afsar, CO-Principal Investigator

I. INTRODUCTION

The purpose of this research was to make use of ultra-high intensity magnetic fields (20 Teslas) and ultra-high resolution spectroscopy in the wavelength region between 1 mm and 0.1 mm to refine and extend existing methods for the identification of residual donors in high-purity epitaxial compound semiconductors. After this was accomplished on GaAs (about 10^{13} donors per cubic centimeter), the method was extended to InP and InGaAs. Finally, our growing understanding of Larsen's extensive theoretical work made it clear that we could also contribute to the solutions of two more questions, namely, the magnetic field dependence of the line shape of the photoconductivity signal and the magnetic field dependence of the spin doublet in GaAs by extending the observations and improving their accuracy. Larsen's prediction of the magnetic field dependence of the splitting of the spin doublet was confirmed; the splitting is largely quadratically dependent on magnetic field intensity but with some higher order contributions.

But the other question, the narrowing to the photoconductivity line for the 1s→2p (m=-1) transition in high intensity magnetic fields is not specifically explained by the theory.

The first objective of this research had to be the demonstration of at least one method for the unambiguous identification of at least one donor in epitaxial GaAs. For many year, chemical back-doping had introduced ambiguities. Moreover, the literature contained many clear disagreements among the leading research groups. We have used several obvious and easy ways to clear up some of the identifications and have demonstrated how they can be ultimately all cleared up.

Neutron transmutation doping of GaAs with Se and Ge in a neutron flux was the simplest. This established that the donor identified in the literature as carbon was actually germanium.

Fetterman's early identification of Sn turned out to be correct, however, to four significant figures in both frequency and magnetic field intensity; we chose to verify it so as to demonstrate another easy method for the comparison of different experimenters' findings and the removal from the literature of some disagreements. This was done by generating the "signature curve" for Sn in n-GaAs containing only one measurable donor known to be Sn.

II. THE SIGNATURE CURVE OF A DONOR*

The signature curve for a particular donor is generated by plotting

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* The description of the photoconductivity spectra and the generation of signature curves was described and demonstrated in the Annual Progress Report for 8/1/78 to 7/31/79

the energy of the transition 1s $\rightarrow$ 2p(m=-1) transition vs magnetic field intensity. At least four significant figures in both variables should be held in order to reslove the signature curves of different donors. All signature curves of donors in a given host are parallel to each other although the curve is not quite a straight line at high fields (field intensities above the linear splitting of the 2p level). The transition is Landau-like at high field and is subject to the nonparabolicity of the conduction band. There are many unique uses for signature curves after they have been established for each donor in a given host: (1) comparison of measurements among different resarch laboratories; (2) quality control in subsequent engineering applications; (3) identification of useful experimental points below noise levels; (4) elimination of data due to phenomena other than donor 1s $\rightarrow$ 2p transitions; and (5) the "shift" of all donor signature curves caused by phenomena (such as strain) arising in the host.

A. COMPARISON OF MEASUREMENTS AMONG DIFFERENT RESEARCH LABORATORIES

If one publishes only a single point with four figure accuracy in energy and magnetic field intensity for the 1s $\rightarrow$ 2p (m=-1) transition as Fetterman did for Sn, one can hardly expect another experimental team in another laboratory to reproduce those parameters identically while using different equipment some years later. Thus our continuous curve of the dependence of the 1s to $2p_-$ energy on magnetic field intensity permitted us to plot Fetterman's point on the graph of the signature curves without having to "calibrate" precisely on Fetterman's experimental system. Indeed, his point did lie on our signature curve for Sn; it showed that the measurements made within two different laboratories could be compared

even though the work was done ten years later and used entirely different types of apparatus.

B. QUALITY CONTROL IN SUBSEQUENT ENGINEERING APPLICATIONS

In a batch process for the production of high purity epitaxial semiconductors for device applications, a spot check can be plotted on the signature curves to identify the residual donors.

C. IDENTIFICATION OF DATA POINTS BELOW THE NOISE LEVEL

A donor that is present in relatively low concentration will not provide a strong 1s to 2p photoconductivity line and can not ordinarily be distinguished from the noise. If this "noise" line can be found at different values of magnetic field, however, and plotted on an existing signature curve, evidence for the existence and approximate concentration of that donor is not altogether lacking.

D.ELIMINATION OF DATA POINTS DUE TO OTHER PHENOMENA

Data points that do not generate a characteristic donor signature curve can be elimated from consideration when attempting to identify the residual donors that are actually present. An occasional spectrum has contained weak points that generated a curve having a different slope and shape. In this case, these points could be set aside but if one had not generated signature curves of real donors, the "single point" spectroscopy technique would require some assignment to be made for this spurious point.

E. SIGNATURE CURVE SHIFT

If a specimen contains three donors such as silicon, sulfur and germanium and all three signature curves have shifted in energy or magnetic field, even in the fourth significant figure, one has ample evidence on which to base an investigationfor sample-related or calibration-related difficulty.

III. TRANSMUTATION DOPING*

Neutron transmutation doping is so common, it is carried out commercially for doping silicon with phosphorous. We doped GaAs with Se and Ge. The "before and after" spectra showed the additional lines for the two donors after which the signature curves were generated. The donor identified in the literature as carbon fell on the germanium signature curve. It was later shown by Theis, Bajaj, Litton and Spitzer that carbon, although amphoteric, enters predominately on the As site, making carbon an acceptor rather than a donor. This explains why we never found or reported carbon as a donor.

IV.THE mbe METHOD FOR IDENTIFYING SINGLE DONORS**

Chemical back doping has often been misleading because unintended donors are sometimes introduced when the intended donor is not introduced. This is caused by differences in segregation coefficient. We suffered from this inconvenience one time when an attempt was made to int-oduce sulfur into GaAs by the vapor phase epitaxy method. No trace of sulfur was found ultimately. It should be noted, however, that high quality epitaxial GaAs made by the molecular beam epitaxy method always comes out p-type, if not deliberately doped. Thus one can introduce a single donor during mbe growth only to the extent necessary to turn the specimen n-type. The Bell Laboratories mbe group headed by A.Y.Cho found no difficulty in doing this and we verified their Sn donor as the only donor present in

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*This topic was discussed at the end of the annual progress report for 8/1/78 to 7/31/79 and in the annual technical report for 8/1/79 to 7/31/80.

**This topic was described in the annual technical report for 8/1/80 to 7/31/81

detectable quantity. Since Fetterman's Sn point fell on Cho's Sn signature curve, there has never been any further disagreement about Sn. If this were done for each donor, one by one, the remaining disagreements could be set aside, one by one.

V. SPLITTING OF THE SPIN DOUBLET*

David Larsen had calculated the spin splitting of the donor electron in GaAs and predicted that the dependence on magnetic field intensity would be larger than quadratic. Unpublished experimental data by Korn had clearly confirmed that the splitting was at least quadratic but the data was not sufficiently accurate to confirm the significance of higher order terms (if any) in magnetic field intensity. Our most recent measurements of the $1s \rightarrow 2p(m=+1)$ transition resolve the splitting and confirm the quadratic term and proves the existence of a measurable contribution from at least one higher order term.

VI. LINE SHAPE OF THE $1s \rightarrow 2p\ (m=-1)$ IN GaAs and InP**

The photoconductivity line at moderate magnetic field intensity is highly asymmetric. It has a sharp edge on the high frequency side and a long tail on the low frequency side. As the magnetic field intensity is increased, the long tail is suppressed until, at abbut 20 Teslas, the line is nearly symmetrical. We have observed the same phenomenon in high purity InP at fields up to 10 Teslas but the line begins to become broad again as the magnetic field intensity is increased toward 20 Teslas.

*This topic was described in the annual technical report 9/1/81 to 8/31/82

**This topic was described for GaAs in the annual technical report 8/1/79 to 7/31/80

This was observed in an excellent specimen of InP obtained from S.H.Groves. It contained only one detectable donor. This was the last investigation begun under this Grant.

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